

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
30 November 2000 (30.11.2000)

PCT

(10) International Publication Number
WO 00/71606 A1

(51) International Patent Classification⁷: C08G 77/42,
77/442, C08F 283/12, 293/00, A61K 7/06

(21) International Application Number: PCT/EP00/04225

(22) International Filing Date: 8 May 2000 (08.05.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
9912077.6 24 May 1999 (24.05.1999) GB

(71) Applicant (for AE, AU, BB, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, SD, SG, SL, SZ, TT, TZ, UG, ZA, ZW only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant (for all designated States except AE, AU, BB, CA, CY, GB, GD, GH, GM, IE, IL, IN, KE, LC, LK, LS, MN, MW, NZ, SD, SG, SL, SZ, TT, TZ, UG, ZA, ZW): UNILEVER NV [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for IN only): HINDUSTAN LEVER LIMITED [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, 400 020 Mumbai (IN).

(72) Inventors: ADAMS, Gerald; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). KHOSHDEL, Ezat; Unilever Research Port Sunlight, Quarry Road East, Bebington,

Wirral, Merseyside CH63 3JW (GB). MORETTA, Anthony; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). PLANT, Yvonne, Christine; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). REID, Euan, Stuart; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB).

(74) Agent: GRIFFITHS, Helen, Sarah; Unilever PLC, Patent Department, Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).

(81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 00/71606 A1

(54) Title: POLYSILOXANE BLOCK COPOLYMERS IN TOPICAL COSMETIC AND PERSONAL CARE COMPOSITIONS

(57) Abstract: A process for making a polysiloxane block copolymer which is built up from units of the formula [A] [B], in which A is a polymeric block built up from radically polymerisable monomer, and B is a polysiloxane block, the process comprising the steps of forming a polysiloxane macroinitiator by grafting a radical initiator onto a polysiloxane via a nucleophilic displacement reaction between groups on the polysiloxane and radical initiator respectively, and reacting the polysiloxane macroinitiator so obtained with radically polymerisable monomers in an atom transfer radical polymerisation reaction to form a polysiloxane block copolymer. Also provided are cosmetic and personal care compositions, such as hair styling compositions, containing the polysiloxane block copolymers.

- 1 -

POLYSILOXANE BLOCK COPOLYMERS IN TOPICAL COSMETIC AND
PERSONAL CARE COMPOSITIONS

5 Field of the Invention

The present invention relates to polysiloxane block
copolymers suitable for use in cosmetic and personal care
compositions, their preparation, and to cosmetic and
10 personal care compositions, such as hair styling
compositions, containing the polysiloxane block copolymers.

Background and Prior Art

15 Cosmetic and personal care compositions such as hair styling
sprays, mousses, gels and shampoos, frequently contain
resins, gums and adhesive polymers to provide a variety of
benefits, for example, film-forming ability, thickening,
sensory properties and hair shaping and setting.

20

Polymers for use in such compositions include organic or
silicone-containing linear or graft copolymers which contain
various monomers in an alternating, random, block or
homopolymer configuration.

25

Graft copolymers are known for use as film-forming polymers
in hair care and other personal care compositions. These
graft copolymers typically comprise a polymeric backbone and
one or more macromonomers grafted to the backbone, in which
30 the physical and chemical attributes such as glass
transition temperature and water solubility can be selected

- 2 -

independently for the polymeric backbone and macromonomer grafts in order to provide the desired overall polymer properties.

- 5 For example, WO95/01383 and WO95/01384 describe the use of water or alcohol soluble or dispersible graft copolymers in hair and skin care compositions, in which the copolymer has a backbone and two or more polymeric side chains, and is formed by copolymerisation of randomly repeating monomer
- 10 units A and B. Monomer A is selected to have a hydrophobic character and macromonomer B comprises a long hydrophilic part. EP 412,704, EP 408,313 and EP 412,707 have suggested the use of silicone grafted acrylate copolymers in hair care applications. US 4,988,506 describes the use of non-pressure
- 15 sensitive polysiloxane-grafted copolymers in hair care compositions.

- Block copolymers have an advantage over graft copolymers in that the polymer architecture can be controlled more
- 20 closely. This is particularly important when designing polymers with segments of distinct physical and chemical properties for particular applications, e.g. alternating "hard" and "soft" segments in a hairspray polymer for improved hold and feel.

- 25 US 5,468,477 describes cosmetics and personal care compositions containing a vinyl-silicone graft or block copolymer comprising a silicone polymer segment and a vinyl polymer segment. This block or graft copolymer is prepared
- 30 by the radical polymerisation of a mercapto functional silicone chain transfer agent and vinyl monomers. Copolymers

- 3 -

prepared by this method generally have a low molecular weight and a low silicone content due to premature chain termination. Also, intramolecular cross-linking reactions lead to polymer build up in an uncontrolled manner, and
5 hence polydisperse systems with a mixture of chain lengths and molecular architectures. Furthermore, the presence of mercapto groups is a disadvantage in personal care applications since they tend to decompose to give odour problems.

10

Another approach to the synthesis of block copolymers is to use organopolysiloxane macroinitiators, which are organopolysiloxanes which contain groups which form radicals. These are described in US 5,523,365 and used in
15 WO98/48771, where a polydimethylsiloxane macroinitiator with azo groups is used to synthesise a block copolymer. Problems include the expense and safety hazards associated with the radical macroinitiator, which has to present in significant quantities, otherwise there will be insufficient siloxane
20 content in the final product. Furthermore, the size of the polydimethylsiloxane macroinitiator means that the reaction is inefficient, and large quantities of unreacted silicone have to be removed in a time-consuming extraction process that would be extremely difficult to scale up.

25

A need exists for conveniently prepared and cost-effective polysiloxane block copolymers for use in cosmetics and personal care compositions.

30 The present invention provides an improved process for making polysiloxane block copolymers in which radical

- 4 -

macroinitiators are prepared from organopolysiloxanes using a simple nucleophilic displacement reaction. The macroinitiators so produced may then be used in atom transfer radical polymerisation to prepare polysiloxane block copolymers of controlled architecture. Atom transfer radical polymerisation is described in general in *Polymer* Vol 39, No.21, pp 5163-5170 (Nakagawa et al) and used in WO98/51261 to make graft copolymers.

10 Summary of the Invention

In a first aspect, the present invention provides a process for making a polysiloxane block copolymer which is built up from units of the formula [A][B], in which A is a polymeric block built up from radically polymerisable monomer, and B is a polysiloxane block, the process comprising the steps of forming a polysiloxane macroinitiator by grafting a radical initiator onto a polysiloxane via a nucleophilic displacement reaction between groups on the polysiloxane and radical initiator respectively, and reacting the polysiloxane macroinitiator so obtained with radically polymerisable monomers in an atom transfer radical polymerisation reaction to form a polysiloxane block copolymer.

25

In a second aspect, the invention provides a polysiloxane block copolymer which is obtainable by the process described above.

- 5 -

The invention also provides a cosmetic and personal care composition, such as a hair styling composition, comprising the polysiloxane block copolymer as described above.

5 Detailed Description and Preferred Embodiments

Process

The process of the present invention comprises two key
10 reaction steps:

First reaction step

The first reaction step involves forming a polysiloxane
15 macroinitiator by grafting a radical initiator onto a polysiloxane via a nucleophilic displacement reaction between groups on the polysiloxane and radical initiator respectively.

20 Typically the polysiloxane macroinitiator is formed by a nucleophilic displacement reaction between:

(i) a polysiloxane which is end-capped with at least one group capable of nucleophilic attack via its O, N or S atom,
25

and

(ii) a radical initiator comprising at least one
- C (O) X group, in which X is a leaving group capable
30 substitution by the nucleophilic O, N or S atom of polysiloxane (i), and at least one organic halide group

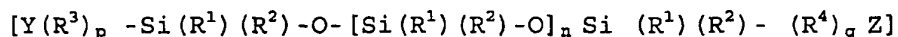
- 6 -

capable of generating a radical in the presence of a transition metal catalyst.

The polysiloxane (i) may be linear, branched or
5 hyperbranched, provided it is end-capped with at least one group as described above. By "end-capped" is meant that the group is at or near a terminal position of the polysiloxane.

Examples of preferred polysiloxanes have the formula:

10



in which n is an integer of 5 to 1,000,000;

15 R^1 and R^2 are independently selected from monovalent, optionally substituted, linear or branched C_{1-18} hydrocarbon radicals,

R^3 and R^4 are independently selected from divalent,
20 optionally substituted, linear or branched $C_1 - C_{18}$ hydrocarbon radicals;

p and q are integers having a value of 0 or 1, and

25 Y and Z are independently selected from hydroxyl, $-NH_2$ and $-NHR^5$ where R^5 is a monovalent, optionally substituted, linear or branched C_{1-18} hydrocarbon radical. Either, but not both, of Y and Z may also be hydrogen, or a monovalent, optionally substituted, linear or branched C_{1-18} hydrocarbon radical
30 thereby giving a mono-end-capped polysiloxane.

- 7 -

Examples of monovalent, unsubstituted radicals are alkyl radicals, such as the methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl and tert-pentyl radical; alkoxy radicals, such as the
5 methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, isobutoxy, tert-butoxy, n-pentoxy, iso-pentoxy, neo-pentoxy and tert-pentoxy radical; hexyl radicals, such as the n-hexyl radical; alkenyl radicals, such as the vinyl, allyl, 5-hexenyl, 4-vinylcyclohexyl and the 3-norbornenyl radical;
10 cycloalkyl radicals, such as cyclopentyl, cyclohexyl, 4-ethylcyclohexyl and cycloheptyl radical; norbornyl radicals and methylcyclohexyl radicals; aryl radicals, such as the phenyl, biphenyl, naphthyl, anthryl and phenanthryl radical; alkaryl radicals, such as o-, m- and p-tolyl
15 radical, xylyl radicals and ethylphenyl radical; and aralkyl radicals, such as the benzyl, styryl, and phenylethyl radicals.

Examples of monovalent, substituted radicals are halogenated
20 hydrocarbon radicals, such as the chloromethyl, 3-chloropropyl, 3-bromopropyl, 3,3,3-trifluoropropyl and 5,5,5,4,4,3,3-heptafluoropentyl radical and the chlorophenyl, dichlorophenyl and trifluorotolyl radical; mercaptoalkyl radicals, such as the 2-mercaptoethyl and 3-
25 mercaptopropyl radical; cyanoalkyl radicals, such as the 2-cyanoethyl and 3-cyanopropyl radical; aminoalkyl radicals, such as the 3-aminopropyl, N-(2-aminoethyl)-3-aminopropyl and N-(2-aminoethyl)-3-amino-(2-methyl)propyl radical; aminoaryl radicals, such as the aminophenyl radical;
30 acyloxyalkyl radicals, such as the 3-acryloxypropyl and 3-

- 8 -

methacryloxypropyl radical; and hydroxyalkyl radicals, such as the hydroxypropyl radical.

Preferred monovalent radicals are independently selected
5 from unsubstituted or substituted C₁ to C₆ alkyl radicals or the phenyl radical, in particular the methyl, ethyl, propyl or phenyl radical.

Examples of divalent hydrocarbon radicals are linear or
10 branched saturated alkylene radicals, such as the methylene and ethylene radical, as well as propylene, butylene, pentylene, hexylene, cyclohexylene and octadecylene radicals; alkoxyalkylene radicals such as the methoxyethylene and ethoxyethylene radical; unsaturated
15 alkylene or arylene radicals, such as the hexenylene radical and phenylene radicals; alkarylene radicals such as the methylphenylene and ethylphenylene radical, and alkoxyarylene radicals such as the methoxyphenylene and ethoxyphenylene radical. The divalent hydrocarbon radical R³
20 and R⁴ can be interrupted by divalent radicals, bonded to carbon atoms on both sides, such as -O-, -C(O)O-, -O(O)C-, -CONR⁶-, -NR⁶C(O)- and -C(O)-, where R⁶ is hydrogen or a monovalent, optionally substituted, linear or branched C₁₋₁₈ hydrocarbon radical as described above.

25

Particularly preferred polysiloxanes corresponding to the above general formula have:

n = 5 to 1,000,000, preferably 5 to 500;

30

R¹ and R² = methyl,

- 9 -

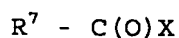
p and q = 0 and Y and Z = hydroxyl; or p and q = 1, R³ and R⁴ = (CH₂)₃ and Y and Z = NH₂ .

The radical initiator (ii) comprises at least one

- 5 - C (O) X group, in which X is a leaving group capable substitution by the nucleophilic O, N or S atom of polysiloxane (i), and at least one organic halide group capable of generating a radical in the presence of a transition metal catalyst.

10

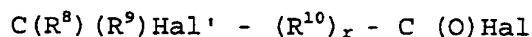
Examples of preferred radical initiators have the formula:



15

where R⁷ is the organic halide group and X is the leaving group. Preferably X is a halogen atom (F, Cl, Br or I). By "organic halide group" is meant any linear, branched or cyclic (aromatic or otherwise) carbon structure, whether
20 substituted or unsubstituted, which also contains a halogen atom (F, Cl, Br or I).

Preferred radical initiators have the general formula:



25

where Hal' and Hal independently denote halogen atoms, R⁸ and R⁹ are independently selected from hydrogen or a monovalent, optionally substituted, linear or branched C₁₋₁₈ hydrocarbon radical as described above, r is an integer having a value of
30 0 or 1, and R¹⁰ is selected from divalent, optionally

- 10 -

substituted, linear or branched $C_1 - C_{18}$ hydrocarbon radicals as described above.

A particularly preferred radical initiator corresponding to
5 the above general formula has:

Hal and Hal' = Br, R^8 and R^9 = methyl and $r = 0$.

The first reaction step involves a nucleophilic displacement
10 reaction between (i) and (ii) under conventional reaction conditions. The nucleophilic O, N or S atom of polysiloxane (i) replaces leaving group X of radical initiator (ii), thereby linking (i) and (ii) to generate a polysiloxane macroinitiator.

15

Second reaction step

The second reaction step involves reacting the organic halide groups of the polysiloxane macroinitiator obtained in
20 step (i) with radically polymerisable monomers in the presence of a catalytic or stoichiometric amount of a Cu (I) salt or other transitional metal species to form a polysiloxane block copolymer.

25 In this reaction step, the organic halide groups act as initiators in the presence of the radically polymerisable monomers and the catalyst, resulting in the linking of a block of radically polymerisable monomers onto the polysiloxane macroinitiator by atom transfer radical
30 polymerisation. This block of radically polymerisable

- 11 -

monomers constitutes the polymeric block (denoted A) of the polysiloxane block copolymer as described above.

The catalyst for the second reaction step is a transition metal salt, preferably a Cu(I) salt such as Cu(I) halide salts (Cl, F, Br, I) and which is preferably complexed to a ligand which is suitable for solubilising the Cu(I) salt in the reaction mixture. WO98/51261 describes preferred ligands for use in solubilising the Cu(I) salt in the reaction mixture (aprotic bidentates such as diphosphates, 2,2' bipyridyl, C₁-C₂₀ alkyl substituted bipyridyl and combinations thereof, most preferably 2,2' bipyridyl complexed to a Cu(I) halide salt, in particular CuCl). WO98/51262 also refers to several journal articles which describe examples of the polymerisation process (atom transfer radical polymerisation) used in the second reaction step of the process of the present invention. Further examples of such descriptions can be found in *Polymer* Vol 39, No.21, pp 5163-5170 (Nakagawa et al) and *Macromolecules* 1997, 30, 2190-2193 (Haddleton et al). Those skilled in the art would understand that a variety of other ligands can also be employed.

The polymerisation process of the second reaction step can be furnished in bulk, solution, emulsion and suspension, as would be understood by those skilled in the art.

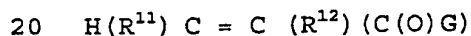
Radically polymerisable monomers suitable for use in the second reaction step of the process of the present invention are preferably ethylenically unsaturated monomers.

- 12 -

By "polymerisable" is meant monomers that can be polymerised in accordance with the second reaction step of the process of the present invention using atom transfer radical polymerisation, more preferably "living" atom transfer radical polymerisation, in which polymer chain length and architecture can be controlled via stability of the radical, thus leading to improved monodispersity.

By "ethylenically unsaturated" is meant monomers that contain at least one polymerisable carbon-carbon double bond (which can be mono-, di-, tri- or tetra -substituted). Either a single monomer or a combination of two or more monomers can be utilised. In either case, the monomers are selected to meet the physical and chemical requirements of the final polysiloxane block copolymer.

Suitable ethylenically unsaturated monomers have the following general formula:



in which R^{11} and R^{12} are independently selected from hydrogen, $C_1 - C_{10}$ straight or branched chain alkyl, methoxy, ethoxy, 2-hydroxyethoxy, 2-methoxyethyl and 2-ethoxyethyl groups;

G is selected from hydroxyl, $-O(M)_{2/v}$, $-OR^{13}$, $-NH_2$, $-NHR^{13}$ and $-N(R^{13})(R^{14})$;

where M is a counter-ion of valency v selected from metal ions such as alkali metal ions and alkaline earth metal ions, ammonium ions and substituted ammonium ions such as

- 13 -

mono-, di-, tri- and tetraalkylammonium ions, and each R^{13} and R^{14} is independently selected from hydrogen, C_1-C_8 straight or branched chain alkyl, N,N-dimethylaminoethyl, 2-hydroxyethyl, 2-methoxyethyl, and 2-ethoxyethyl.

- 5 Representative non-limiting examples of monomers useful herein include protected or non-protected acrylic acid and methacrylic acid and salts, esters and amides thereof.

The salts can be derived from any of the common nontoxic
10 metal, ammonium, or substituted ammonium counter ions. The esters can be derived from C_{1-40} straight chain, C_{3-40} branched chain, or C_{3-40} carbocyclic alcohols, from polyhydric alcohols having from about 2 to about 8 carbon atoms and from about 2 to about 8 hydroxyl groups (non-limiting examples of which
15 include ethylene glycol, propylene glycol, butylene glycol, hexylene glycol, glycerol, and 1,2,6-hexanetriol); from amino alcohols (non-limiting examples of which include aminoethanol, dimethylaminoethanol and diethylaminoethanol and their quaternised derivatives); or from alcohol ethers
20 (non-limiting examples of which include methoxyethanol and ethoxyethanol).

The amides can be unsubstituted, N-alkyl or N-alkylamino mono-substituted, or N,N-dialkyl, or N,N-dialkylamino
25 disubstituted, wherein the alkyl or alkylamino groups can be derived from C_{1-40} straight chain, C_{3-40} branched chain, or C_{3-40} carbocyclic moieties. In addition, the alkylamino groups can be quaternised. Also useful as monomers are protected and unprotected acrylic or/and methacrylic acids,
30 salts, esters and amides thereof, wherein the substituents are on the two and three carbon position of the acrylic

- 14 -

and/or methacrylic acids, and are independently selected from C₁₋₄ alkyl, hydroxyl, halide (-Cl, -Br, -F, -I), -CN, and -CO₂H, for example methacrylic acid, ethacrylic acid, alpha-chloroacrylic acid and 3-cyano acrylic acid. The salts, esters, and amides of these substituted acrylic and methacrylic acids can be defined as described above for the acrylic/methacrylic acid salts, esters and amides. Other useful monomers include vinyl and allyl esters of C₁₋₄₀ straight chain, C₃₋₄₀ branched chain, or C₃₋₄₀ carbocyclic carboxylic acids, vinyl and allyl halides (e.g. vinyl chloride, allyl chloride), (e.g. vinyl pyridine, allyl pyridine); vinylidene chloride; and hydrocarbons having at least one unsaturated carbon-carbon double bond (e.g. styrene, alpha-methylstyrene, t-butylstyrene, butadiene, isoprene, cyclohexadiene, ethylene, propylene, 1-butene, 2-butene, isobutylene, p-methylstyrene); and mixtures thereof.

Preferred monomers useful herein include those selected from protected and unprotected acrylic acid, methacrylic acid, ethacrylic acid, methyl acrylate, ethyl acrylate, n-butyl acrylate, iso-butyl acrylate, t-butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, octyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, iso-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, decyl methacrylate, methyl ethacrylate, ethyl ethacrylate, n-butyl ethacrylate, iso-butyl ethacrylate, t-butyl ethacrylate, 2-ethylhexyl ethacrylate, decyl ethacrylate, 2,3-dihydroxypropyl acrylate, 2,3-dihydroxypropyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, hydroxypropyl methacrylate, glyceryl monoacrylate, glyceryl monoethacrylate, glycidyl

- 15 -

- methacrylate, glycidyl acrylate, acrylamide, methacrylamide, ethacrylamide, N-methyl acrylamide, N,N-dimethyl acrylamide, N,N-dimethyl methacrylamide, N-ethyl acrylamide, N-isopropyl acrylamide, N-butyl acrylamide, N-t-butyl acrylamide,
- 5 N,N-di-n-butyl acrylamide, N,N-diethylacrylamide, N-octyl acrylamide, N-octadecyl acrylamide, N,N-diethylacrylamide, N-phenyl acrylamide, N-methyl methacrylamide, N-ethyl methacrylamide, N-dodecyl methacrylamide, N,N-dimethylaminoethyl acrylamide, quaternised N,N-
- 10 dimethylaminoethyl acrylamide, N,N-dimethylaminoethyl methacrylamide, quaternised N,N-dimethylaminoethyl methacrylamide N,N-dimethylaminoethyl acrylate, N,N-dimethylaminoethyl methacrylate, quaternised N,N-dimethylaminoethyl acrylate, quaternised N,N-dimethylaminoethyl
- 15 methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl ethacrylate, glyceryl acrylate, 2-methoxyethyl acrylate, 2-methoxyethyl methacrylate, 2-methoxyethyl ethacrylate, 2-ethoxyethyl acrylate, 2-ethoxyethyl methacrylate, 2-ethoxyethyl ethacrylate, maleic
- 20 acid, maleic anhydride and its half esters, fumaric acid, itaconic acid, itaconic anhydride and its half esters, crotonic acid, angelic acid, diallyldimethyl ammonium chloride, vinyl pyrrolidone vinyl imidazole, methyl vinyl ether, methyl vinyl ketone, maleimide, vinyl pyridine, vinyl
- 25 furan, styrene sulphonate, allyl alcohol, allyl citrate, allyl tartrate, vinyl acetate, vinyl alcohol, vinyl caprolactam and mixtures thereof.

- More preferred monomers are those selected from methyl
- 30 acrylate, methyl methacrylate, methyl ethacrylate, ethyl acrylate, ethyl methacrylate, ethyl ethacrylate, n-butyl

- 16 -

acrylate, n-butyl methacrylate, n-butyl ethacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, 2-ethylhexyl ethacrylate, N-octyl acrylamide, 2-methoxyethyl acrylate, 2-hydroxyethyl acrylate, N,N-dimethylaminoethyl acrylate,
 5 N,N-dimethylaminoethyl methacrylate, acrylic acid, methacrylic acid, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate and mixtures thereof.

Most preferred monomers are those selected from N,N-dimethylaminoethyl acrylate, N,N-dimethylaminoethyl
 10 methacrylate, 2-ethylhexyl acrylate, hydroxyethyl methacrylate, N-octyl acrylamide, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate and mixtures thereof.

15 Polysiloxane Block Copolymers

A typical polysiloxane block copolymer obtainable by the process described above is built up from units of the general formula [A]L[B], in which A is a polymeric block
 20 built up from radically polymerisable monomer, B is a polysiloxane block and L is a divalent linker group which links the A and B blocks via O-Si, N-Si or S-Si bonds to the B block. Preferably L is selected from:

25 - R¹⁵ - C (O) - O - ;

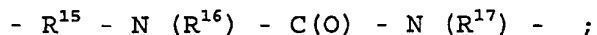
- R¹⁵ - O - C (O) - O - ;

- R¹⁵ - C (O) - N(R¹⁶) - ;

30

- R¹⁵ - O - C(O) - N (R¹⁶) - , or

- 17 -



in which R^{15} is a divalent, optionally substituted, linear or branched $C_1 - C_{18}$ hydrocarbon radical as described above, and

5

R^{16} and R^{17} are independently selected from monovalent, optionally substituted, linear or branched $C_1 - C_{18}$ hydrocarbon radicals as described above.

- 10 The overall molecular architecture of the silicone block copolymers of the invention can be described by the formulas A-L-B, A-L-B-L-A, $-(A-L-B)_n-$, wherein n is an integer of 2 or greater, or $[A-L-][A-L-]B[-L-A][-L-A]$, wherein A-L-B represents a diblock structure, A-L-B-L-A represents a
- 15 triblock structure, $-(A-L-B)_n-$ represents a multiblock structure, and $[A-L-][A-L-]B[-L-A][-L-A]$ represents a dendritic structure.

Cosmetic and Personal Care Compositions

20

- The polysiloxane block copolymers of the present invention are preferably formulated into hair care compositions, especially hairspray compositions, but can also be formulated into a wide variety of product types, including
- 25 mousses, gels, lotions, tonics, sprays, shampoos, conditioners, rinses, hand and body lotions, facial moisturisers, sunscreens, anti-acne preparations, topical analgesics, mascaras, and the like. The carriers and additional components required to formulate such products
- 30 vary with product type and can be routinely chosen by one

- 18 -

skilled in the art. The following is a description of some of these carriers and additional components.

Carriers

- 5
- Hair care compositions of the present invention can comprise a carrier, or a mixture of such carriers, which are suitable for application to the hair. The carriers
- 10 are present at from about 0.5% to about 99.5%, preferably from about 5.0% to about 99.5%, more preferably from about 10.0% to about 98.0%, of the composition. As used herein, the phrase "suitable for application to hair" means that the carrier does not damage or negatively affect the aesthetics of hair or cause irritation to the underlying skin. Carriers
- 15 suitable for use with hair care compositions of the present invention include, for example, those used in the formulation of hair sprays, mousses, tonics, gels, shampoos, conditioners, and rinses. The choice of appropriate carrier will also depend on the particular copolymer to be used, and
- 20 whether the product formulated is meant to be left on the surface to which it is applied (e.g., hair spray, mousse, tonic, or gel) or rinsed off after use (e.g., shampoo, conditioner, rinse).
- 25 The carriers used herein can include a wide range of components conventionally used in hair care compositions. The carriers can contain a solvent to dissolve or disperse the particular copolymer being used, with water, the C1-C6 alcohols, lower alkyl acetate and mixtures thereof
- 30 being preferred. The carriers can also contain a wide variety of additional materials such as acetone,

- 19 -

hydrocarbons (such as isobutane, hexane, decene),
halogenated hydrocarbons (such as Freons) and volatile
silicon derivatives such as cyclomethicone. When the hair
care composition is a hair spray, tonic, gel, or mousse the
5 preferred solvents include water, ethanol, volatile silicone
derivatives, and mixtures thereof. The solvents used in such
mixtures may be miscible or immiscible with each other.
Mousses and aerosol hair sprays can also utilise any of the
conventional propellants to deliver the material as a foam
10 (in the case of a mousse) or as a fine, uniform spray (in
the case of an aerosol hair spray). Examples of suitable
propellants include materials such as
trichlorofluoromethane, dichlorodifluoromethane,
difluoroethane, dimethylether, propane, n-butane or
15 isobutane. A tonic or hair spray product having a low
viscosity may also utilise an emulsifying agent. Examples of
suitable emulsifying agents include nonionic, cationic,
anionic surfactants, or mixtures thereof. If such an
emulsifying agent is used, it is preferably present at a
20 level of from about 0.01% to about 7.5% of the composition.
The level of propellant can be adjusted as desired but is
generally from about 3% to about 30% of mousse compositions
and from about 15% to about 50% of the aerosol hair spray
compositions.

25

Suitable spray containers are well known in the art and
include conventional, non-aerosol pump sprays i.e.,
"atomisers", aerosol containers or cans having
propellant, as described above, and also pump aerosol
30 containers utilising compressed air as the propellant.

- 20 -

Where the hair care compositions are conditioners and rinses the carrier can include a wide variety of conditioning materials. Where the hair care compositions are shampoos, the carrier can include, for example, surfactants, suspending agents, and thickeners.

The carrier can be in a wide variety of forms. For example, emulsion carriers, including oil-in-water, water-in-oil, water-in-oil-in-water, and oil-in-water-in-silicone emulsions, are useful herein. These emulsions can cover a broad range of viscosities, e.g., from about 100 cps to about 200,000 cps. These emulsions can also be delivered in the form of sprays using either mechanical pump containers or pressurised aerosol containers using conventional propellants. These carriers can also be delivered in the form of a mousse. Other suitable topical carriers include anhydrous liquid solvents such as oils, alcohols, and silicones (e.g., mineral oil, ethanol, isopropanol, dimethicone, cyclomethicone, and the like); aqueous-based single phase liquid solvents (e.g., hydro-alcoholic solvent systems); and thickened versions of these anhydrous and aqueous-based single phase solvents (e.g., where the viscosity of the solvent has been increased to form a solid or semi-solid by the addition of appropriate gums, resins, waxes, polymers, salts, and the like).

Additional Components

A wide variety of additional components can be employed in cosmetic and personal care compositions according to the present invention. Examples include the following:

- 21 -

- sunscreening agents such as 2-ethylhexyl
p-methoxycinnamate, 2-ethylhexyl N,N-dimethyl-p-
aminobenzoate, p-aminobenzoic acid, 2-phenylbenzimidazole-5-
sulfonic acid, octocrylene, oxybenzone, homomenthyl
5 salicylate, octyl salicylate, 4,4'-methoxy-t-
butyldibenzoylmethane, 4-isopropyl dibenzoylmethane, 3-
benzylidene camphor, 3-(4-methylbenzylidene) camphor,
titanium dioxide, zinc oxide, silica, iron oxide, and
mixtures thereof.
- 10
- anti-dandruff actives such as zinc pyrithione,
piroctone olamine, selenium disulphide, sulphur, coal tar,
and the like.
- 15 - conditioning agents for hair care compositions such as
hydrocarbons, silicone fluids, and cationic materials. The
hydrocarbons can be either straight or branched chain and
can contain from about 10 to about 16, preferably from about
12 to about 16 carbon atoms. Examples of suitable
20 hydrocarbons are decane, dodecane, tetradecane, tridecane,
and mixtures thereof. Examples of suitable silicone
conditioning agents useful herein can include either cyclic
or linear polydimethylsiloxanes, phenyl and alkyl phenyl
silicones, and silicone copolyols. Cationic conditioning
25 agents useful herein can include quaternary ammonium salts
or the salts of fatty amines.
- surfactants for hair shampoo and conditioner
compositions. For a shampoo, the level is preferably from
30 about 10% to about 30%, preferably from 12% to about 25%, of
the composition. For conditioners, the preferred level of

- 22 -

surfactant is from about 0.2% to about 3%. Surfactants useful in compositions of the present invention include anionic, nonionic, cationic, zwitterionic and amphoteric surfactants.

5

- carboxylic acid polymer thickeners. These crosslinked polymers contain one or more monomers derived from acrylic acid, substituted acrylic acids, and salts and esters of these acrylic acids and the substituted acrylic acids, wherein the crosslinking agent contains two or more carbon-carbon double bonds and derived from a polyhydric alcohol. Examples of carboxylic acid polymer thickeners useful herein are those selected from the group consisting of carbomers, acrylates/C10-C30 alkyl acrylate crosspolymers, and mixtures thereof. Compositions of the present invention can comprise from about 0.025% to about 1%, more preferably from about 0.05% to about 0.75% and most preferably from about 0.10% to about 0.50% of the carboxylic acid polymer thickeners.

20

- emulsifiers for emulsifying the various carrier components of the compositions of the invention. Suitable emulsifier types include polyethylene glycol 20 sorbitan monolaurate (Polysorbate 20), polyethylene glycol 5 soya sterol, Steareth-20, Cetareth-20, PPG-2 methyl glucose ether distearate, Ceteth-10, Polysorbate 80, cetyl phosphate, potassium cetyl phosphate, diethanolamine cetyl phosphate, Polysorbate 60, glyceryl stearate, PEG-100 stearate, and mixtures thereof. The emulsifiers can be used individually or as a mixture of two or more and can comprise from about 0.1% to about 10%, more preferably from about 1%

30

- 23 -

to about 7%, and most preferably from about 1% to about 5% of the compositions of the present invention.

- vitamins and derivatives thereof (e.g., ascorbic acid,
5 vitamin E, tocopheryl acetate, retinoic acid, retinol, retinoids, and the like.

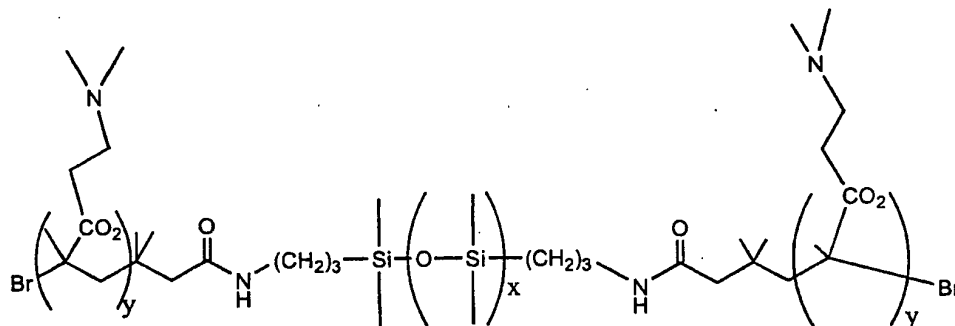
- cationic polymers (e.g., cationic guar gum derivatives such as guar hydroxypropyltrimonium chloride and
10 hydroxypropyl guar hydroxypropyltrimonium chloride, available as the Jaguar C series from Rhone-Poulenc).

- preservatives, antioxidants, chelators and sequestrants; and aesthetic components such as fragrances, colourings,
15 hair nutrients and essential oils.

The invention will now be illustrated by the following non-limiting Examples:

EXAMPLESExamples 1-8

- 5 ABA Triblock copolymers of the following general formula:



PDMAEMA-PDMS-PDMAEMA ABA TRIBLOCK

- 10 were prepared by atom transfer radical polymerisation (ATRP). Commercially available polydimethyl siloxanes (PDMS) - amine propyl terminated were halide functionalised to give an effective ATRP initiator. Controlled molecular weights were achieved with narrow polydispersities.

- 25 -

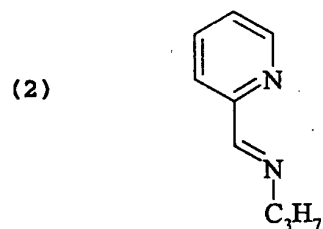
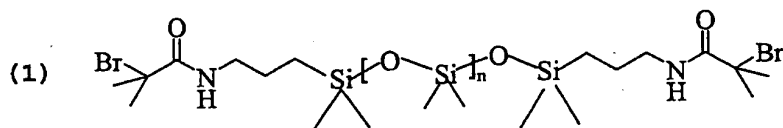
EXAMPLE	Mwt of Initiator	Value of x	Mwt of DMAEMA	Value of y	Total Mwt of Polymer
1	3300	45	10000	64	13300
2	3300	45	4000	25	7300
3	3300	45	6000 (NMR)	40	9300
4	2000	27	15000 (NMR)	95	17000
*5	800	7	10000	64	10800
6	3300	45	4700 (NMR)	30	8000
*7	800	7	10000	64	10800
8	3300	45	10000	64	13300

*Examples 5 and 7 were prepared using an ester PDMS initiator rather than the pictured amide PDMS initiator, giving an - O - linkage in place of the pictured - (CH₃)₂ -NH- linkage in the final polymer.

- 26 -

Preparation Method

Cu^IBr (0.2732g, 1.905mmol) along with a magnetic stirrer bar was placed in a dry Schlenk flask which was then evacuated and flushed with nitrogen three times. 2-dimethylaminoethyl methacrylate (3.9mL, 0.023moles), toluene (7.2mL) and the PDMS initiator (1) (2g, 0.952mmol) were added to the Schlenk using degassed syringes.* The solution was then deoxygenated by three freeze-pump-thaw cycles. Finally, once the flask had reached the desired reaction temperature of 90°C the n-propyl-2-pyridinalmethanimine ligand (2) (0.54mL, 3.809mmol) was added with stirring. The reaction mixture immediately turned dark brown in colour on addition of the ligand.



*Target molecular weight of DMAEMA blocks = 4000, molecular weight of initiator = 2000 (total = 6000). The ratio of [monomer] : [initiator] determines molecular weight of end polymer. In the described ATRP the required ratio of

- 27 -

[monomer] : [initiator] = 25 : 1. The ratios for the other listed reagents are as follows; $[\text{Cu}^{\text{I}}\text{Br}]$: [Initiator] = 1:2, [Ligand] : $[\text{Cu}^{\text{I}}\text{Br}]$ = 2:1 and solvent volume : monomer volume = 2:1.

5

The monomer was purified by passing down a basic alumina column prior to use and purged with nitrogen for at least one hour. Toluene, which was used as a solvent for all polymerisations, was also degassed in this manner. $\text{Cu}^{\text{I}}\text{Br}$ was
10 purified before use according to a published procedure.¹

1) Keller, R. N.; Wyckoff, H. D. *Inorganic Synthesis*, 1947, 2,1.

15 Purification of polymer

The resultant dark brown solution was passed down an alumina column several times using a conventional solvent such as dichloromethane or tetrahydrofuran. When the solution
20 appeared colourless the solvent was removed under vacuum to yield a pale yellow solid.

- 28 -

ResultsFilm Forming

- 5 A solution of ethanol / water (55%:45%) was made up. A small sample of polymer (0.5g) was added to the solution (10 mL). Some samples needed agitation but others dissolved straight away. A small quantity of solution (1mL) was placed in a plastic dish and left to dry for 3 hours.

- 29 -

EXAMPLE	FILM FORMING PROPERTIES	SOLUBILITY			
		100% water	100% ethanol	55% ethanol/water	100% Methyl Acetate
1	non tacky clear flexible	soluble	soluble	soluble	soluble
2	slightly yellow non tacky flexible	soluble	soluble	soluble	soluble
3	non tacky clear flexible	soluble	soluble	soluble	soluble
4	non tacky clear flexible	soluble	soluble	soluble	soluble
5	non tacky clear flexible	soluble	soluble	soluble	soluble
6	slightly yellow non tacky flexible	soluble	soluble	soluble	soluble
7	slightly yellow non tacky brittle	soluble	soluble	soluble	insoluble
8	slightly yellow non tacky brittle	soluble	soluble	soluble	insoluble

Bond strength analysis

5

Diastron MTT600 parameters: % extension = 100
 Rate (mm/min) = 10
 Max force (g) = 200
 Gauge force (gmf) = 2

- 30 -

5% aqueous alcohol solution (55% ethanol/water):

1 microlitre pipetted onto junction

Temperature = 20°C

5 Humidity = 50%

- 31 -

EXAMPLE	BOND STRENGTH (g)	EXTENSION (%)
1	36.88 50.88 20.88 AVE = 42.53g 50.63 ST.DEV = 13.7 53.38	2.79 6.89 4.19 AVE = 6.76% 10.27 ST.DEV = 2.9 7.68
2	29.25 * * AVE = 26.29g 23.75 ST.DEV = 2.77 25.88	2.23 AVE = 2.45% 2.58 ST.DEV = 0.19 2.55
3	31.38 * * AVE = 31.42g 30.38 ST.DEV = 1.06 32.50	4.14 AVE = 4.17% 4.60 ST.DEV = 0.42 3.76
4	* 20.50 27.50 AVE = 25.78 29.88 ST.DEV = 4.00 25.25	2.83 4.77 AVE = 3.79% 4.75 ST.DEV = 1.12 2.82

5

10

- 32 -

EXAMPLE	BOND STRENGTH (g)	EXTENSION (%)
5	56.00 26.00 45.25 AVE = 42.42g 43.88 ST.DEV = 15.20 40.38	6.23 3.21 5.55 AVE = 5.00% ST.DEV = 1.58
6	* * 7.5 AVE = 11.96g 16.63 ST.DEV = 4.56 11.75	1.89 AVE = 1.57 % 1.59 ST.DEV = 0.33 1.24
7	* * 24.13 AVE = 19.50g 22.00 ST.DEV = 6.26 12.38	4.73 AVE = 3.41% 3.24 ST.DEV = 1.25 2.25
8	* * 10.63 AVE = 14.79g 23.50 ST.DEV = 7.54 12.38	1.26 AVE = 1.61% 2.60 ST.DEV = 0.87 0.96

Sensory

5

The polymer of Example 1 was formulated into a 55% VOC
pumpspray(4.2% resin , 55% ethanol, 40.8% water)

This was sprayed on to a switch and compared against the
commercial product Suave ® Extra Hold(4.2% AMPHOMER ®)

10 pumpspray.

- 33 -

The formulation with Example 1 had major wins on softness and least deposits(both before and after brushout).

- 34 -

CLAIMS

1. A process for making a polysiloxane block copolymer which is built up from units of the formula [A][B], in which A is
5 a polymeric block built up from radically polymerisable monomer, and B is a polysiloxane block, the process comprising the steps of forming a polysiloxane macroinitiator by grafting a radical initiator onto a polysiloxane via a nucleophilic displacement reaction
10 between groups on the polysiloxane and radical initiator respectively, and reacting the polysiloxane macroinitiator so obtained with radically polymerisable monomers in an atom transfer radical polymerisation reaction to form a polysiloxane block copolymer.
- 15
2. A process according to claim 1, comprising the steps of:
- (a) forming a polysiloxane macroinitiator by a nucleophilic substitution reaction between:
- 20
- (i) a polysiloxane which is end-capped with at least one group capable of nucleophilic attack via its O, N or S atom,
- and
- 25
- (ii) a radical initiator comprising at least one - C (O) X group, in which X is a leaving group capable of substitution by the nucleophilic O, N or S atom of polysiloxane (i), and at least one organic halide group
30 capable of generating a radical in the presence of a transition metal catalyst;

- 35 -

followed by

(b) reacting the organic halide groups of the polysiloxane macroinitiator so obtained with radically polymerisable monomers in the presence of a catalytic amount of a Cu (I) salt or other transitional metal species to form a polysiloxane block copolymer.

3. A polysiloxane block copolymer obtainable by the process of claim 1 or 2.

4. A polysiloxane block copolymer according to claim 3, which is built up from units of the general formula [A]L[B], in which A is a polymeric block built up from radically polymerisable monomer, B is a polysiloxane block and L is a divalent linker group which links the A and B blocks via O-Si, N-Si or S-Si bonds to the B block, and which is preferably selected from:

- R¹⁵ - C (O) - O - ;

- R¹⁵ - O - C (O) - O - ;

- R¹⁵ - C (O) - N(R¹⁶) - ;

- R¹⁵ - O - C(O) - N (R¹⁶) - , or

- R¹⁵ - N (R¹⁶) - C(O) - N (R¹⁷) - ;

in which R¹⁵ is a divalent, optionally substituted, linear or branched C₁ - C₁₈ hydrocarbon radical, and

- 36 -

R^{16} and R^{17} are independently selected from monovalent, optionally substituted, linear or branched C_{1-18} hydrocarbon radicals.

5 5. A cosmetic and personal care composition comprising the polysiloxane block copolymer of claim 3 or 4.

6. A cosmetic and personal care composition according to claim 5, which is formulated as a hairspray, gel or mousse.

10

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/04225

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G77/42 C08G77/442 C08F283/12 C08F293/00 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G C08F A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>NAKAGAWA Y ET AL: "Development of novel attachable initiators for atom transfer radical polymerization. Synthesis of block and graft copolymers from poly(dimethylsiloxane) macroinitiators" POLYMER,GB,ELSEVIER SCIENCE PUBLISHERS B.V., vol. 39, no. 21, 1 October 1998 (1998-10-01), pages 5163-5170, XP004139649 ISSN: 0032-3861 cited in the application page 5163, left-hand column, paragraph 1 -page 5169, left-hand column, paragraph 3; figures; examples</p> <p style="text-align: center;">--- -/--</p>	1-6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

20 July 2000

Date of mailing of the international search report

31/07/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Hutton, D

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/04225

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 98 01480 A (UNIV CARNEGIE MELLON) 15 January 1998 (1998-01-15) page 35, line 11 -page 38, line 20; examples 14-16,19,23,24 -----	1-6
Y	WO 98 51261 A (PROCTER & GAMBLE) 19 November 1998 (1998-11-19) cited in the application the whole document -----	1-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/04225

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9801480 A	15-01-1998	US 5789487 A	04-08-1998
		AU 3585997 A	02-02-1998
		BR 9710273 A	10-08-1999
		CA 2259995 A	15-01-1998
		CN 1228789 A	15-09-1999
		EP 0914352 A	12-05-1999
		US 5945491 A	31-08-1999
WO 9851261 A	19-11-1998	AU 7073798 A	08-12-1998
		EP 0977540 A	09-02-2000
		ZA 9804087 A	16-11-1998